Pyrolysis of Waste Plastics Using Synthesized Catalysts from Fly Ash

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ABSTRACT

Waste plastics can be converted into fuel oil by pyrolysis using suitable catalysts. Waste plastics attributed to the olefin series are more difficult to pyrolyze than any other thermoplastics for production of fuel oil because of their bonding structures and cracking patterns. Fly ash obtained from the coal combustion was used as catalysts for the pyrolysis of waste plastics including PE and PP of olefin series after the pre-treatment by NaOH.. These synthesized catalysts were more effective for PP than for PE which is difficult to pyrolyze. They also increase the pyrolysis effects to bring down the decomposition temperature and time. These experimental results in case of using synthesized catalysts were compared with the results in case of using other catalysts. Experimental results showed that synthesized catalysts from fly ash can be used for the pyrolysis of most of waste plastics including the olefin series to make fuel oil.

Introduction

Waste plastics can be reused as valuable resources according to the treatment technologies. The mechanical recycles for the production using the same material can be recommended as a desirable technology because this makes no more pollution problems. But it is very difficult to separate various waste plastics with dust and metals into one-component raw material which can be recycled without any problems. So thermal recycle technologies are the objects of interest as alternatives for the mechanical recycle technologies.

In these technologies, pyrolysis may be favorably used for oil and monomer recovery from waste plastics. Also, this technology has more advantages than combustion technology in the view of discharging less pollutants. Especially, it can be more attractive in majority countries including Korea with high oil price than any other technologies because it is able to make light oil to be directly used for the industrial fuel.

But, all kinds of plastics attributed to the series of thermoplastics is not easily converted into oil product by pyrolysis. To pyrolyze plastics such as polyethylene(PE) and polypropylene(PP) of olefin series, the catalysts with high cracking property are needed.

Other plastics including acrylonitrile-butadiene-styrene(ABS) and polystyrene(PS) can be easily pyrolyzed under the lower temperature than PE and PP without catalysts for the production of light oil.

In this research, the waste plastics of olefins such as polyethylene(PE) and polypropylene(PP) were pyrolyzed to compare the catalytic effects each other in the batch reactor. The yields of pyrolysis oil from PE and PP were 75 ~89% in case of using the cracking catalysts such as synthesized catalyst from fly ash(SCF), HY zeolite, Mordenite and silica-alumina(S-A). Also, these product oil were analyzed by the simulated distillation gas chromatography (SIMDIS GC)for comparing the characteristics of pyrolysis oil made under the various conditions.

Table 1 shows the trends of production of waste plastics. The consumption rates of plastics go up rapidly and their quantities reach to three million tons per year in 1996. The order of production quantity of waste plastics is PP> HDPE> LDPE>PVC> PS> ABS. In these plastics, PVC is mostly in the industrial use and is rarely produced from municipal wastes.

<Table 1> Tendencies of Production on the Types of Waste Plastics in Korea (Unit : 1,000 t)

Type / Year	LDPE	HDPE	PP	PVC	PS	ABS	Sum
1988	302	109	180	196	71	32	890
1990	342	160	234	179	48	50	1,013
1991	345	218	294	196	84	60	1,197
1993	380	392	457	307	170	57	1,763
1994	442	442	538	317	184	46	2,017
1996	-	-	-	-	-	-	3,020

Experiment

Experimental apparatus is shown in Figure 1. The mechanical agitator was installed in the batch type reactor wrapped around with electric heater for controlling the pyrolysis temperature of waste plastic. The organic vapor pyrolyzed from waste plastics can pass the catalytic cracker bed or not when catalyst is charged with waste plastics in the reactor. After that, the vapor is discharged through 1st and 2nd condenser for product oil conversion. These two condensers are maintained at different temperatures, 70 and 10 .

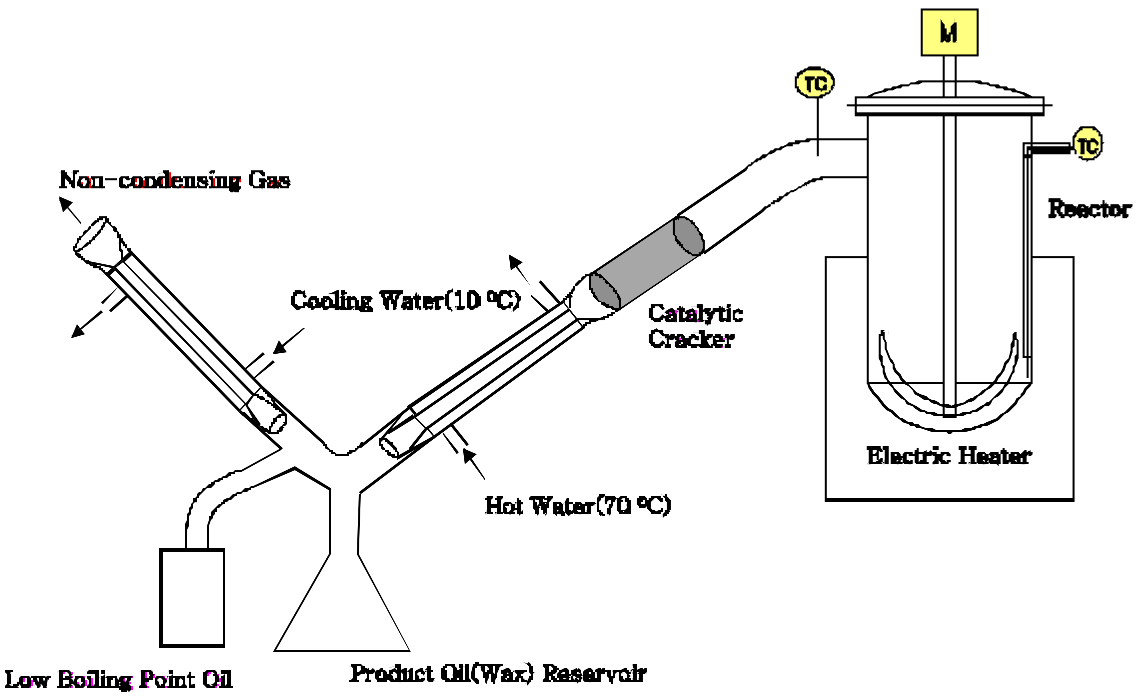

Figure 1 Batch Type Reactor for Pyrolysis of Waste Plastics

Pyrolysis oil collected from each condenser was analyzed by SIMDIS GC to investigate the catalytic properties and the pyrolysis conditions.

Table 2 shows chemical compositions of the catalysts and fly ash obtained from coal fired power plants. To use fly ash as synthesized catalyst it was treated in NaOH solution for more 24 hrs, washed by distilled water and dried. To make another synthesized catalysts this catalyst can be impregnated in the nickel nitrate solution. So two types of catalysts were made for the pyrolysis of PE and PP of olefin series.

<Table 2 > chemical compositions of the catalysts

Component	Mordenite	HY	Silica Alumina	Fly Ash
SiO_2	91.7	74.9	87	53.56
Al_2O_3	8.23	24.0	13	27.71
Na_2O_3	0.03	1.1	-	0.37
Fe	-	0.03	-	5.53
SiO_2/Al_2O_3(-)	18.9	5.31	6.69	1.93

Results and Discussion

Figure 2 shows the pyrolysis properties without any catalyst. We can find the pyrolysis of LDPE occur rapidly during the short elapsed time of 15 minutes. The initiation temperature is around 450 and the terminal temperature around 510 .

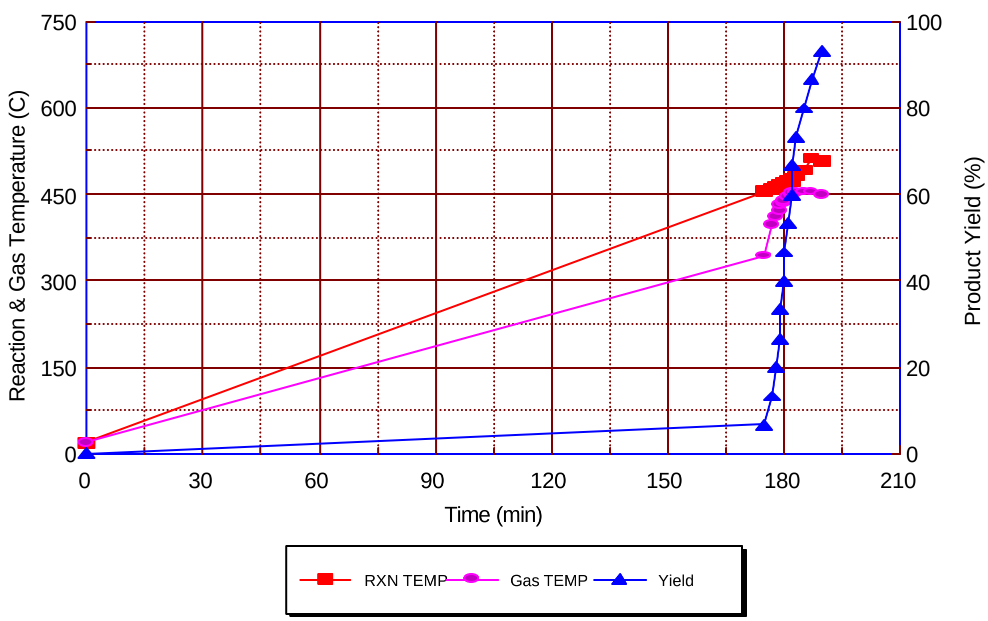

Fig. 2 Pyrolytic Properties of LDPE without Catalyst

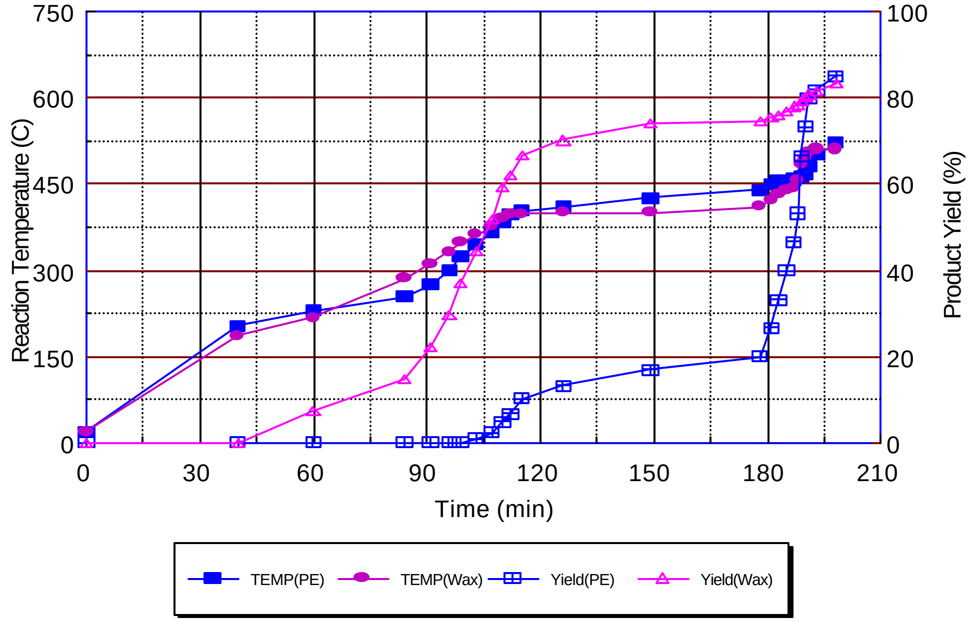

Figure 3 Pyrolytic Properties of LDPE and LDPE Wax on Uses of HY

But, Figure 3 shows the different pyrolytic effects on using catalyst of HY. In this case the catalyst was charged with sample for the pyrolysis. We can find the catalyst gives positive effects for the decrease of pyrolysis time and temperature. Also, wax product after the pyrolysis was re-pyrolyzed with HY catalyst for the comparison of catalytic effects. Wax can be more easily pyrolyzed than original sample. This implies that wax is transformed to lower molecular product by first pyrolysis and easier in pyrolyzing object material than the original sample.

From Figure 4, we can find that the synthesized catalyst from fly ash is more effective to pyrolyze LDPE of olefin series than no catalyst. This can be proven from the comparisons of pyrolyzed temperature and yield change shown in Figure 2 and Figure 4. The required time for the initiation of pyrolysis in case of using SCF is more shortened than in case of no catalyst. But the final yield of the former case is not high. Also, the catalyst of impregnated NiO into fly ash increases the pyrolysis effects to decompose the bonding structure. These results can be easily compared in the change of boiling point distribution of product oil to represent the pyrolytic characteristics.

Figure 5 shows the pyolyisis characteristics of PP without catalyst. Here, we can see different properties from the pyrolysis of LDPE in Figure 2. PP is relatively easier to

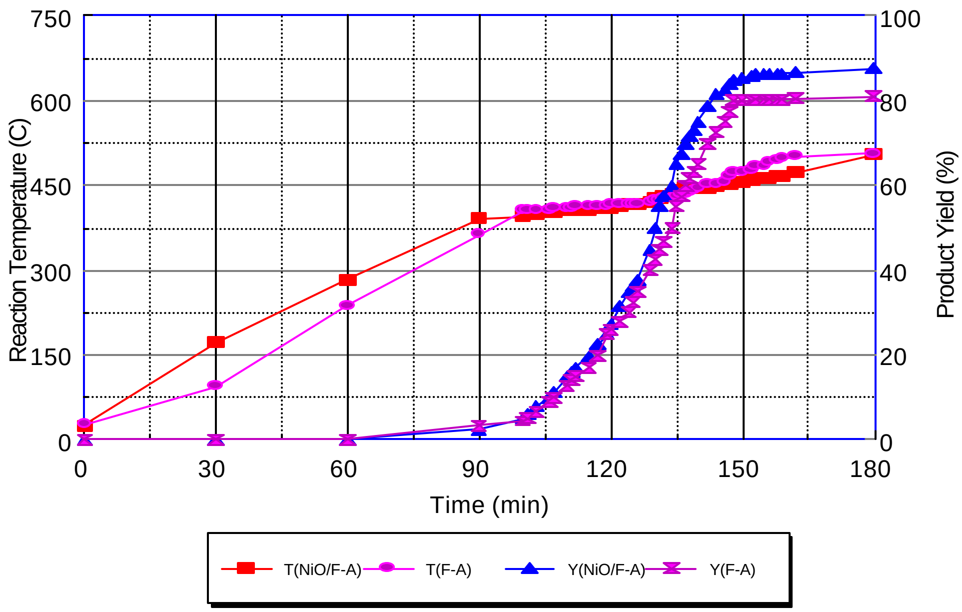

Figure 4 Comparison of Pyrolytic Properties of LDPE with NiO/Fly Ash and Fly Ash

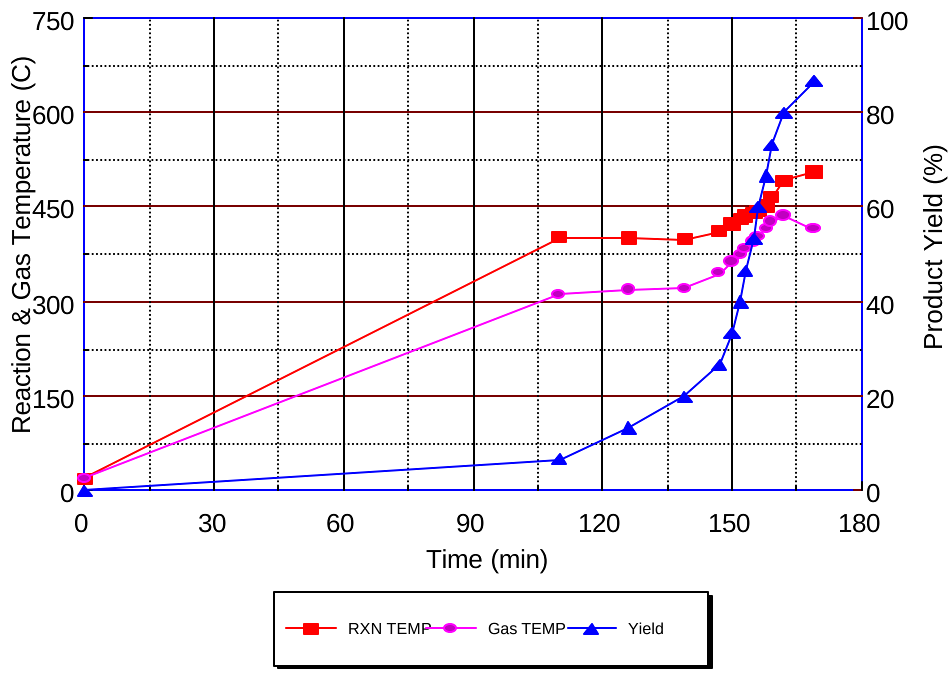

Fig. 5 P yrolytic Properties of PP without Catalyst

pyrolyze than PE because of less strong bonding force with methyl group. Accordingly, the pyrolysis temperature and time of PP were more decreased to 500 and 150 min than those of LDPE.

To compare the catalytic effects by SFC, PP was pyrolyzed with fly ash catalyst produced after the treatment of NaOH and impregnated NiO into fly ash made by the former method. Figure 6 shows those results which are different from the case of using no catalyst in Figure 5.

The cracking patterns of PP by NiO/F-A and F-A are very similar. But NiO/F-A is slightly better in the view of product yield and forms more light oil than F-A.

The boiling point distributions of LDPE product oil from various conditions are shown in Figure 7. These data were acquired by SIMDIS. This Figure says that the pyrolysis oil by catalyst is much lighter than that by no catalyst. The mark of reverse triangle(▼) indicates the boiling point distribution of diesel oil. Below about 50 mass %, all the product oil have the lower boiling points than that of diesel oil. But, above 50 mass %, the pyrolysis oil produced by SFC have higher boiling points than that of diesel. So these product oil appeared to be wax or cream phase. But, the product oil from silica alumina catalyst can meet the boiling point range of diesel. The color of this product oil is light yellow.

The pyrolysis oil produced from PP of the same olefin series as PE is relatively lighter than PE pyrolysis oil. Only the product oil by no catalyst has higher boiling point distribution than that of diesel. Except for this product, the other product oil pyrolyzed by three types of catalyst satisfy the boiling point ranges of diesel. Especially it can be shown that two types of product oil by SFC can be used as an alternative fuel oil without problem from this Figure.

1. Accordingly, fly ash acquired after the burning of coal can be used as a synthesized catalyst for the pyrolysis of PP to make fuel oil. But to obtain the product oil as an alternative oil from PE, further researches are more needed hereafter to modify the characteristics of SFC

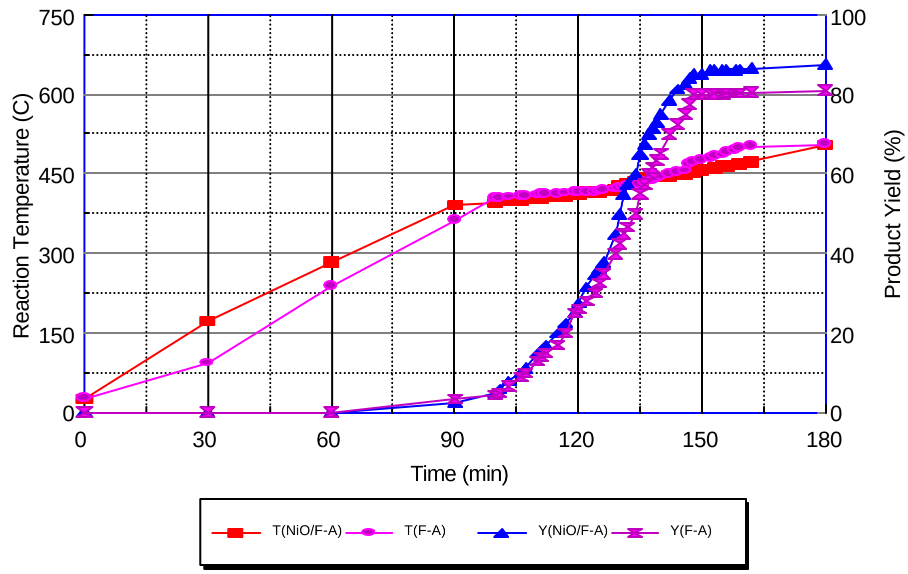

Figure 6 Comparison of Pyrolytic Properties of PP with SFC and No Catalyst

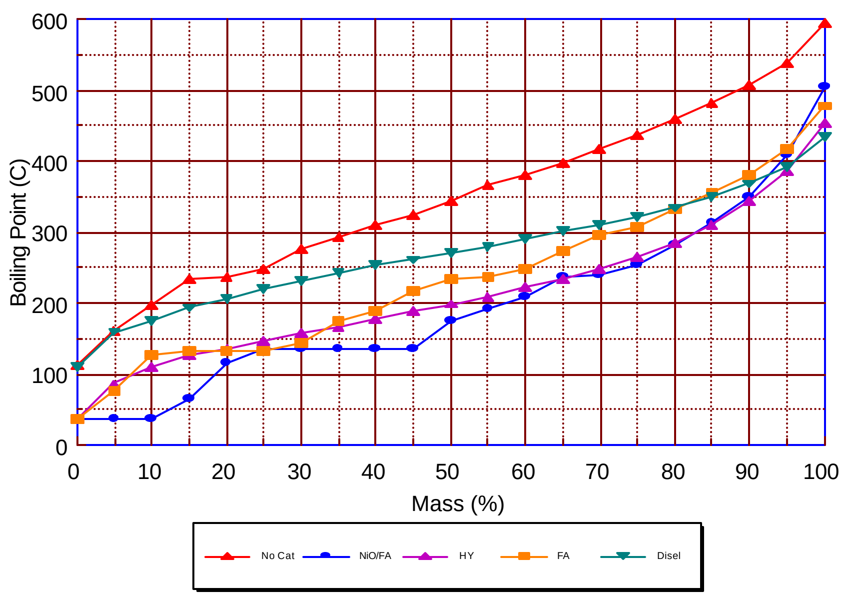

Fig. 7 Boiling Point Distribution of LDPE Pyrolysis Oil Produced by Types of Catalysts

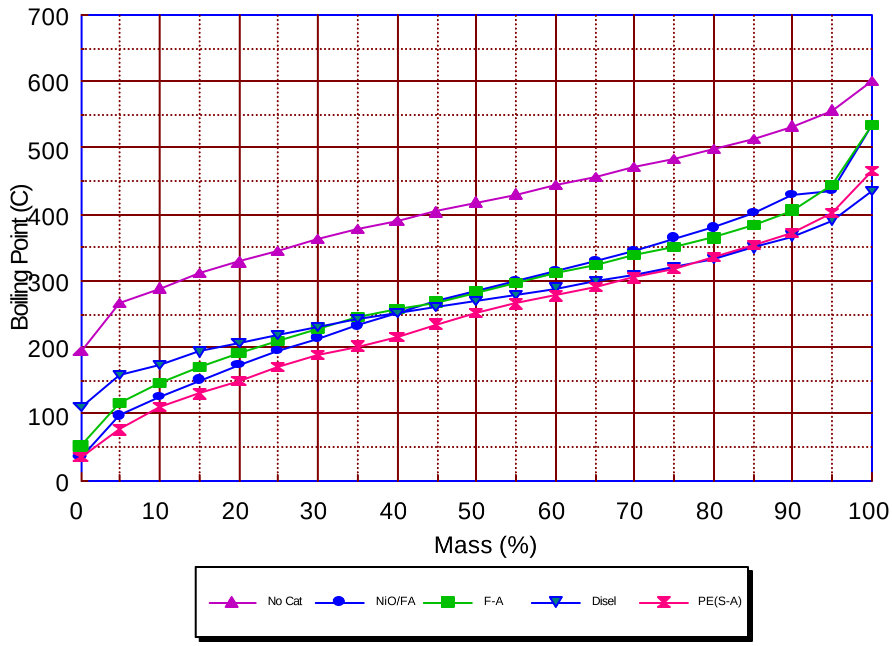

Figure 8 Boiling Point Distribution of PP Pyrolysis Oil Produced by Types of Catalysts

Conclusion

Summary of the results on the pyrolysis researches of waste plastics using synthesized fly ash catalysts (SFC) are as follows:

1. By using SFC for the pyrolysis of waste plastics of olefin series, the pyrolysis effects were considerably improved in decreasing the decomposition temperature and the initiation time for pyrolysis by about 30 and 30 min, respectively.
2. For the pyrolysis of PE, SFC was somewhat more effective than some zeolite catalysts or no catalyst. But the pyrolysis oil produced by SFC appeared to be creamy phase and was not in the full boiling point range of diesel.
3. In case of pyrolyzing PP by SFC, better oil was made for the alternative fuel oil which can be used without problem as commercial diesel oil.

4. Fly ash produced after burning of coal was confirmed as a catalyst after its appropriate treatment. Also, it was checked by the X-ray diffraction analysis for SFC

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